AD-A166 885 CHEMISTRY OF NEW SILICON CONTAINING POLYMERS TRIPLY BONDED SILICON INTERM (U) UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT OF CHEMITT W P WEBER 1/1

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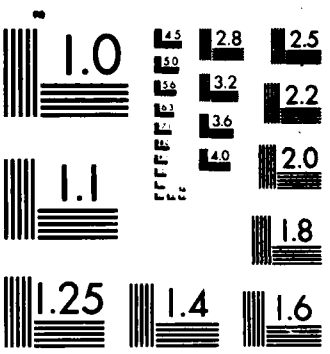

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William P. Weber

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A method to generate [O=Si=O] in the gas phase by flash vacuum pyrolysis (FVP) of 2,3:4,7 diepoxy 5-silaspiro [4.4[nonane was developed. Reactive pi-bonded silicon nitrogen double bonds intermediates were generated by FVP of dimethoxymethylsilyl-bis (trimethylsilyl) amine. Photolysis of dodecamethylcyclohexasilane yields both dimethylsilylene and methylsilene. The oxidation of dimethylsilylene with sulfoxides yields silanones.

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PROGRESS REPORT #6 / FINAL REPORT

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Triply Bonded Silicon Intermediates

Principal Investigator: William P. Weber

Loker Hydrocarbon Research Institute

Department of Chemistry

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University Park

Los Angeles, California 90089-1661

COMPLETED PROJECT SUMMARY

1. TITLE: Chemistry of New Silicon Containing Polymers Triply Bonded Silicon Intermediates

2. PRINCIPAL INVESTIGATOR: Professor William P. Weber

3. INCLUSIVE DATES: August 31, 1982 to October 31, 1985

4. GRANT NUMBER: AFOSR 82-0333

5. COSTS AND FY SOURCE:

6. SENIOR RESEARCH PERSONNEL:

Professor W. P. Weber, principal investigator worked on this contract ten percent of his time during the academic years 8-31-1982 to 10-31-1985 and one hundred percent of his time for two months each Summer 1983, 1984, and 1985.

Professor K. L. Servis worked one month during the Summer 1984 as a consultant on ^{29}Si NMR.

Professor Kyung Tae Kang, on sabbatical leave from the Department of Chemistry of Pusan University, Pusan, South Korea, has worked on this contract 1-15-1985 to 10-31-1985.

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Dr. S. Kazoura, 9-1-1983 to 5-31-1984. Dr. Kazoura received his Ph.D. from USC under my supervision.

Dr. Y. M. Pai, 2-1-1985 to 10-31-1985. Dr. Pai received his Ph.D. from USC under my supervision.

Dr. E. Wanek, 3-3-1983 to 6-30-1984. Dr. Wanek is a graduate of the Technical University, Graz, Austria.

Dr. A. Bacereido, 8-1-1985 to 10-31-1985. Dr. Bacereido is a graduate of the Universite Paul Sabatier, Toulouse, France.

7. JUNIOR RESEARCH PERSONNEL:

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J. Mullis, 8-31-1982 to 8-31-1983, and 6-1-1984 to 8

Y. M. Pai, 8-31-1982 to 8-31-1983, and 6-1-1984 to 12-

G. Henry, 6-1-1983 to 8-31-1983, 6-1-1984 to 8-31-1984, and 6-1-1985 to 10-31-1985.

S. Carr, 6-1-1983 to 8-31-1983, and 6-1-1984 to 1-15-1985.

S. Hedayati, 6-1-1983 to 8-31-1983.

E. Marslett, 6-1-1984 to 8-31-1984.

C. Juengst, 10-1-1984 to 10-31-1985.

C. P. Kuan, 6-1-1985 to 8-31-1985.

UNDERGRADUATE RESEARCH ASSISTANTS:

D. Dowd, 5-30-1984 to 7-25-1984

C. Smith, 5-31-1984 to 6-27-1984

8. PUBLICATIONS:

1. Deoxygenation of Dialkyl Sulfoxides by Dimethylsilylene, A Mechanistic Study, Ibrahim Saleh Alnaimi and William P. Weber, J. Organometal. Chem., 241, 171 (1983).

2. Selectivity in the Reactions of Alkyl Lithium Reagents with α,ω-Dichloropermethylsiloxanes, Samih Amine Kazoura and William P. Weber, J. Organometal. Chem., 243, 149 (1983).

3. Oxidation of Dodecamethylcyclohexasilane by meta-Chloroperbenzoic Acid, Ibrahim Saleh Alnaimi and William P. Weber, Organometallics, 2, 903 (1983).

4. Photolysis of Polysilanes, William P. Weber, in Ultrastructure Processing of Ceramics, Glasses and Composites, edited by L.L. Hench and D.R. Ulrich, J. Wiley (1984), pp. 292-306.

5. Flash Vacuum Pyrolysis of Dimethoxymethylsilyl-bis(trimethylsilyl)-amine: 1,3-Sigmatropic Rearrangement of Silaimine Intermediates, Samih Amine Kazoura and William P. Weber, J. Organometal. Chem., 268, 19 (1984).

6. Co-pyrolysis of Dimethoxysilyl-bis(trimethylsilyl)amine and Hexamethylcyclotrisiloxane-1,3-sigmatropic Rearrangements of Silaimine Intermediates, Samih Amine Kazoura and William P. Weber, J. Organometal. Chem., 271, 47 (1984).

7. Preparation of 1-Silyl and 1,3-bis(silyl)adamantanes, Yi-Ming Pai, Erich Wanek and William P. Weber, J. Organometal. Chem., 270, 271 (1984).

8. Thermolysis of 6-Oxa-3-Sila Bicyclo[3,1,0]hexanes: A New Convenient Route to Silicon-Oxygen π-Bonded Species, G. Manuel, G. Bertrand,

W.P. Weber and S.A. Kazoura, Organometallics, 3, 1340 (1984).

9. Photolysis of Dodecamethylcyclohexasilane - Formation of Both Methylsilene and Dimethylsilylene, I.S. Alnaimi, W.P. Weber, A.S. Nazran, and D. Griller, J. Organometal. Chem., 272, C10 (1984).

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11. Unsaturated Reactive Intermediates in Organosilicon Chemistry-Recent Results, W.P. Weber, S.A. Kazoura, G. Manuel and G. Bertrand, in "Organosilicon and Bioorganosilicon Chemistry", edited by H. Sakurai, Ellis Horwood Publishers, 1985, p. 99-106; Invited Lecture, 7th International Silicon Symposium, Kyoto, Japan, September 13, 1984.

12. Silicon-29 NMR Studies of Polymethylhydrosiloxanes: T_1 Measurements, Yi-Ming Pai, William P. Weber and Kenneth L. Servis, J. Organometal. Chem., 288, 269 (1985).

13. Titanium Tetrachloride Promoted Reactions of Allylic Trimethylsilanes and Oxetane, Steve A. Carr and William P. Weber, J. Org. Chem., 50, 2782 (1985).

14. Preparation of Oligomeric and Polymeric α,ω-bis(Trimethylsiloxy)-polymethylchlorosiloxanes and Their Reactions with Alkyllithium Reagents, Yi-Ming Pai, Kenneth L. Servis and William P. Weber, Organometallics, in press (1986).

15. Adamantyldimethyl Ethers, Erich Wanek, Yi-Ming Pai and William P. Weber, Synthesis Communications, 15, 185 (1985).

16. Silicon Dioxide [O=Si=O]: New Routes to Cyclic Spirosiloxanes; Chemical Vapor Deposition of SiO_2, J. Wiley & Sons, in press;

Invited Lecture, 2nd International Symposium on Ultrastructure Processing of Ceramics, Glasses and Composites, February 25-March 1, 1985.

17. Zinc Iodide Catalyzed Reactions of Oxetanes with Trimethylsiyl Cyanide, Steve A. Carr and William P. Weber, Synthesis Communication, 15, 775 (1985).

18. $Co_2(CO)_8$ Catalyzed Reactions of Styrene Oxide with Trialkylsilanes, Kyung Tae Kang and William P. Weber, Tetrahedron Lett., 5415 (1985).

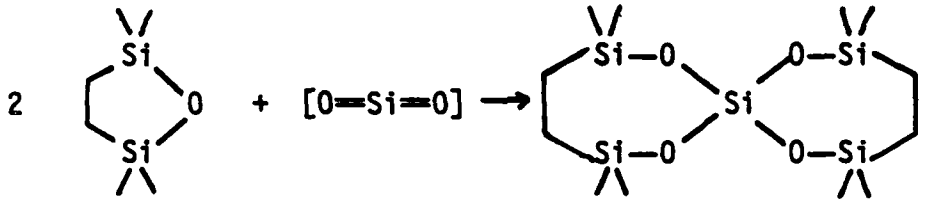
19. $Co_2(CO)_8$ Catalyzed Reaction of Oxetanes with Trialkylsilanes, Kyung Tae Kang and William P. Weber, Tetrahedron Lett., 5753 (1985).

20. Deuterium Isotope Effects on Silicon-29 Chemical Shifts, Fabienne Berchier, Yi-Ming Pai, William P. Weber and Kenneth L. Servis, Mag. Reson. Chem., in press (1986).

21. Generation of Silicon Dioxide [O=Si=O] by Flash Vacuum Pyrolysis, George K. Henry, Robert Bau, Georges Manuel and William P. Weber, Organometallics, submitted (1985).

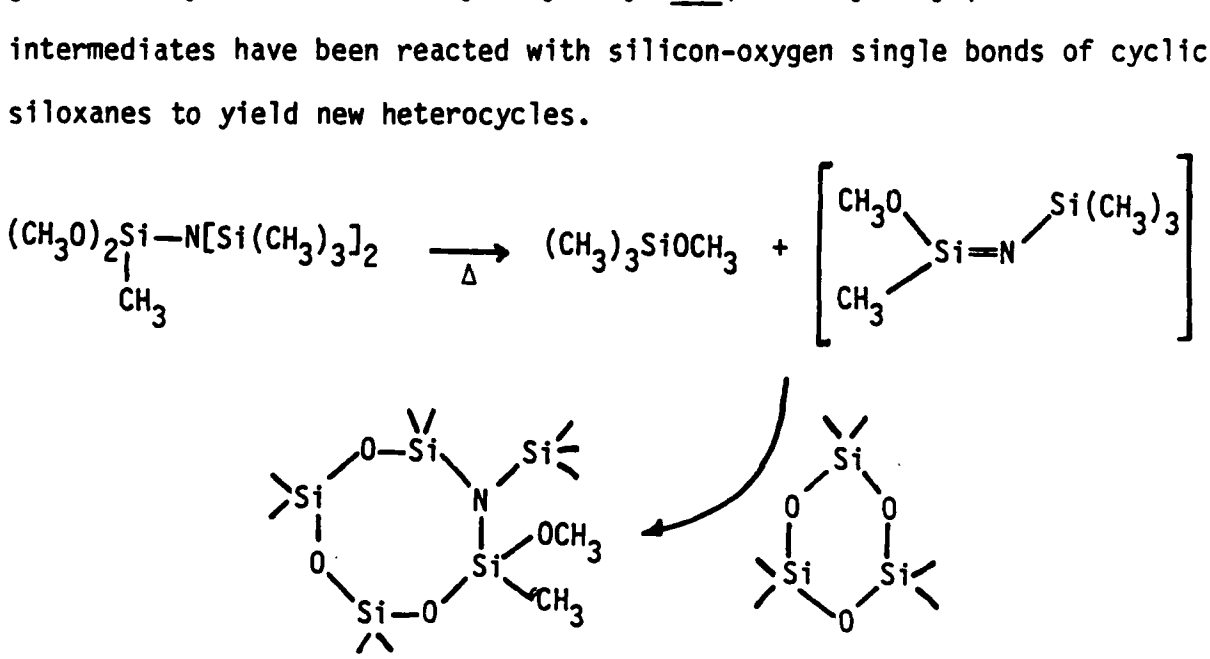
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A method to generate [O=Si=O] in the gas phase by flash vacuum pyrolysis of 2,3:4,7 diepoxy 5-silaspiro [4.4] nonane (I) has been developed. Co-pyrolysis of I and cyclic siloxanes permits the facile synthesis of spirosiloxanes.



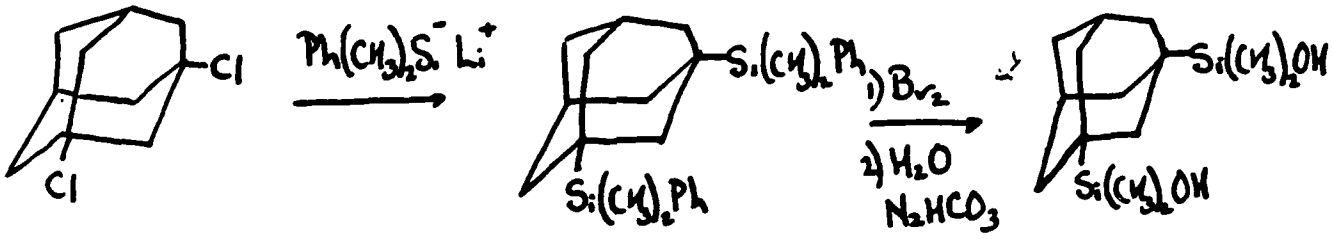
FVP of I alone yields a high surface area (300 M^2/g) silica which has been further characterized by scanning and transmission electron microscopy. See publications 8, 11, 16 and 21

Reactive π-bonded silicon nitrogen double bonds intermediates have been generated by FVP of dimethoxymethylsilyl-bis(trimethylsilyl)amine. These intermediates have been reacted with silicon-oxygen single bonds of cyclic siloxanes to yield new heterocycles.



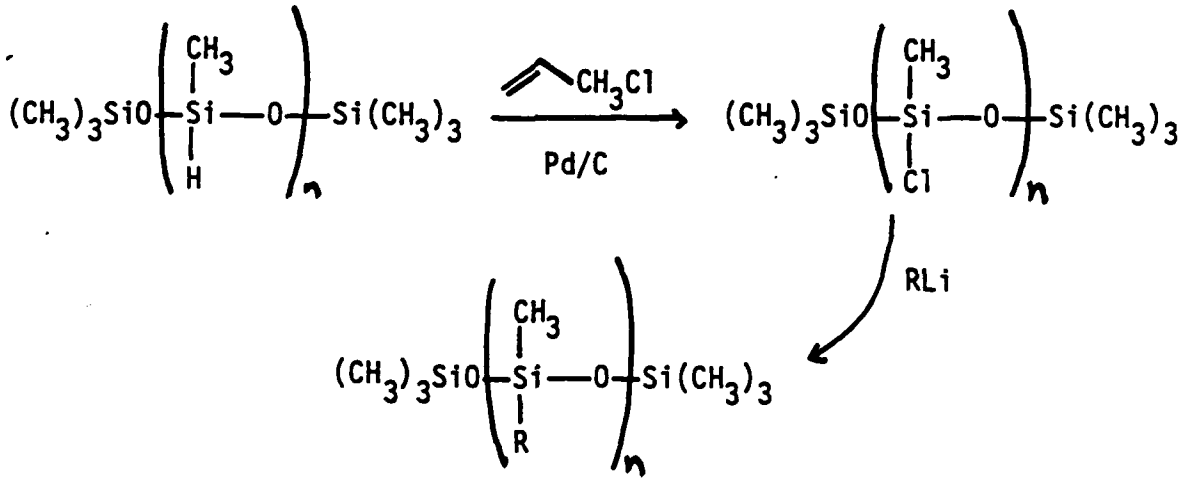
See publications 5, 6 and 11.

We have prepared 1,3-bis(silyl)adamantanes as outlined below.



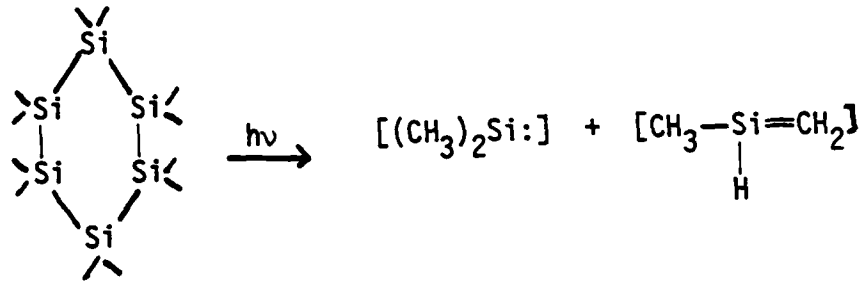
See publications 7 and 15.

We have chlorinated α,ω-bis(trimethylsiloxy)polymethylhydrosiloxane polymers to yield α,ω-bis(trimethylsiloxy)polymethylchlorosiloxanes. These reactive polymers have been reacted with alkyl lithium reagents to yield α,ω-bis(trimethylsiloxy) polyalkylmethylsiloxanes.

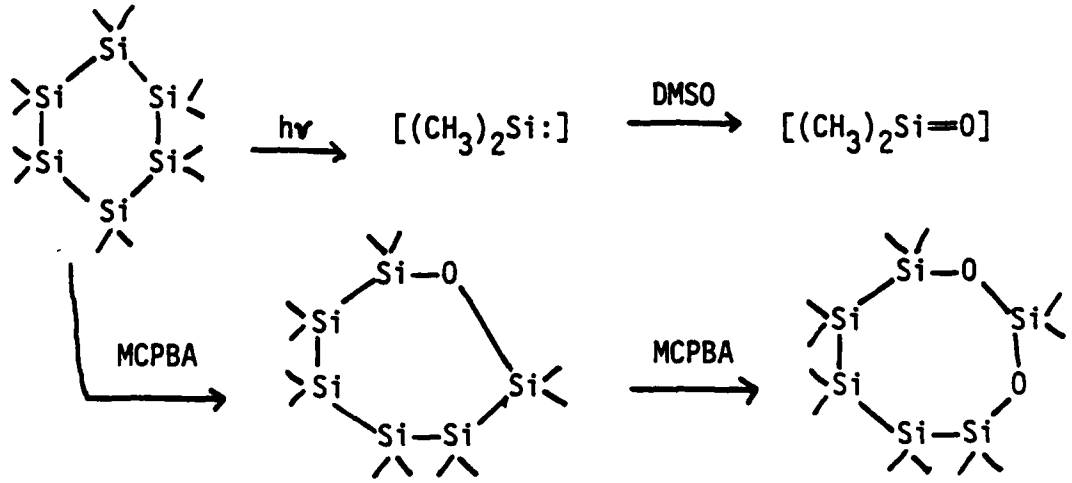


See publications 2 and 14.

We have found that photolysis of dodecamethylcyclohexasilane (II) yields both dimethylsilylene and methylsilene. The ultraviolet spectra of dimethylsilylene in solution and the kinetics of its reaction with various substrates have been determined. See publications 9 and 10.

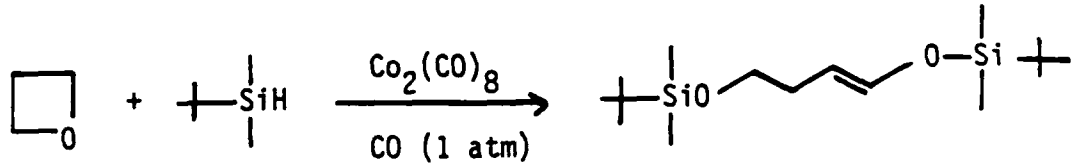


The oxidation of dimethylsilylene with sulfoxides yields silanones. The reaction of m-chloroperbenzoic with II selectively oxidizes Si-Si bonds adjacent to Si-O bonds.



See publications 1 and 3.

We have found that the use of the sterically hindered t-butyldimethylsilane permits control in the silyl hydroformylation reaction.



See publications 18 and 19.

We have utilized ^{29}Si NMR to explore T_1 (relaxation times) of polymethylhydrosiloxane polymers. See publication 12.

Deuterium isotope effects on ^{29}Si chemical shifts have been observed for the first time. See publication 20.

END

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